

# Padina Pavonica Extract as a Green Inhibitor for Brass Corrosion in 0.1 N H<sub>3</sub>PO<sub>4</sub> Solutions

R. Selva Kumar<sup>1\*</sup> S. Gomathi<sup>1</sup> and V. Chandrasekaran<sup>2</sup>

<sup>1</sup> Department of Chemistry, Mahendra Arts & Science College (Autonomous), Kalippatti, Namakkal – 637 501, Tamil Nadu, India.

<sup>2</sup> Department of Chemistry, Govt. Arts College (Autonomous), Salem – 636 007, Tamil Nadu, India.

**ABSTRACT:** The effect of marine alga *Padina pavonica* extract on corrosion inhibition of brass in phosphoric acid was investigated by weight-loss method, potentiodynamic polarization and electrochemical impedance spectroscopic studies. The inhibition efficiency is found to increase with increasing concentration of alga extract and decreases with rise in temperature. The activation energy, thermodynamic parameters (free energy, enthalpy and entropy change) and kinetic parameters (rate constant and half-life) for inhibition process were calculated. These thermodynamic and kinetic parameters indicate a strong interaction between the inhibitor and the brass surface. The inhibition is assumed to occur via adsorption of inhibitor molecules on the brass surface, which obeys Temkin adsorption isotherm. The adsorption of inhibitor on the brass surface is exothermic, physical, and spontaneous, follows first order kinetics. The polarization measurements showed that the inhibitor behaves as a mixed type inhibitor and the higher inhibition surface coverage on the brass was predicted. Inhibition efficiency values were show a good trend follows with weight-loss, potentiodynamic polarization and electrochemical impedance spectroscopy studies. Surface study techniques FT-IR and SEM were carried out to ascertain the inhibitive nature of the algal extract on the brass surface.

**KEYWORDS:** *Padina pavonica*, Inhibition, Corrosion, Brass, Phosphoric acid. SEM. FT-IR

<https://doi.org/10.29294/IJASE.6.2.2019.1351-1360>

© 2019 Mahendrapublications.com, All rights reserved

## 1. INTRODUCTION

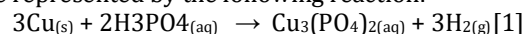
Phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) is a major chemical product, which has many important uses especially in the production of fertilizers. Most of the acid is produced from phosphate rock by wet process. Brass and stainless steel are frequently used in many parts of the wet process and a considerable quantity of data has been published about the resistance of these materials to corrosion by acid solutions [1,2]. Most of the previous studies were focused on the inhibition of metals in HCl or H<sub>2</sub>SO<sub>4</sub> solutions using organic compounds containing N, S, O atoms as corrosion inhibitors [3-5]. Most of the research has been done with naturally occurring substances since they are known to be eco-friendly and with little or no side effects on human. Among the naturally occurring substances reported in the corrosion study of metals like brass, aluminium, tin and mild steel, there are leave extracts, gums and exudates, dyes, oils from plant materials, plant seeds and fruits, and anti-bacterial drugs. Plant extracts like the extract of *Cocos nucifera*-coconut palm-petiole; *Musa Paradisiaca*; *Mentha Pulegium*; *Treculia Africana* leaves and *Lupinus varius* leaves have been studied and established their corrosion inhibition effects [6-10]. They were all found to be good corrosion inhibitors with no effect on the environment.

In the present study, the effect of addition of marine alga *Padina pavonica* extract on the corrosion inhibition of brass in 0.1 N phosphoric acid solutions

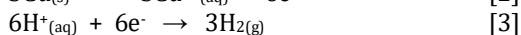
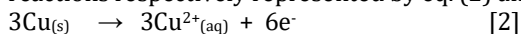
at different temperatures and various time intervals has been investigated by weight-loss method, potentiodynamic polarization and electrochemical impedance spectroscopy studies. The weight loss measurement aimed to predict the inhibition efficiency on brass corrosion and the adsorption isotherm, thermodynamic and kinetic feasibility of inhibition *via* surface coverage on brass by adsorbed extract. The inhibition type and inhibition efficiency were determined from the polarization measurements and impedance spectroscopy studies. Surface analytical techniques (FT-IR and SEM) were carried out to ascertain the inhibitive nature of the algal extract on the brass surface.

### 1.1 Brass Corrosion Mechanism

The dissolution of copper in phosphoric acid can be represented by the following reaction:



This copper dissolution, represented by eq. (1), can be described by anodic and cathodic controlled reactions respectively represented by eq. (2) and (3)



The presence of PO<sub>4</sub><sup>3-</sup> ions (from H<sub>3</sub>PO<sub>4</sub>), increases the rate at which copper corrodes causing the combination of PO<sub>4</sub><sup>3-</sup> ions with Cu (II) ions to form copper phosphate, as shown below

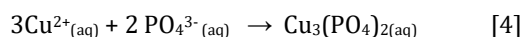
\*Corresponding Author: [drsrk1986@gmail.com](mailto:drsrk1986@gmail.com)

Received: 11.09.2019

Accepted: 18.10.2019

Published on: 30.11.2019

Selva Kumar et al.,



This process represented by eq. (4), releases electrons which cause  $\text{H}^+$  ions to be chemically reduced to hydrogen gas, as shown in eq. (3). There are sacrificial substances known as corrosion inhibitors, which retard the rate at which copper corrodes by decreasing rate(s) at which the anodic and/or cathodic controlled reactions of eq. (2) and (3) occur [11]. Frontier orbital theory suggests that corrosion inhibitors retard metal corrosion effectively if electrons can easily be released by the inhibitors, from their highest occupied molecular orbitals (HOMOs). It is believed that these HOMOs are possessed by rich electron sites on the inhibitors such as: Unsaturation (aromatic centers,  $\text{C}=\text{C}$ ,  $\text{C}=\text{O}$ ,  $\text{N}=\text{O}$  and the likes) and heteroatom (oxygen, nitrogen, sulphur and the likes)[11].

## 2. MATERIAL AND METHODS

### 2.1 Materials

The chemical composition (weight percent) of the brass used in the present study was 71.5 % Cu, 28.38 % Zn, 0.07 % Pb, and 0.05 % Fe. The geometry of the specimens for weight-loss experiments was as follows: length: 5 cm, width: 1 cm, and thickness: 0.3 cm. The brass specimens were polished mechanically with different grades of emery papers (1/0 to 4/0) and were thoroughly washed with double distilled water then degreased in acetone and dried. The solutions were prepared from analar grade chemicals using double distilled water. Phosphoric acid solution was used as a corrosion medium.

The *Padina pavonica* extract (PPE) was extracted with ethanol from marine alga *Padina pavonica* using soxhelt extractor. The alga was collected in the Bay of Bengal, Kanyakumari, South India. The alga was washed with water, dried in air, protected from light, for two weeks. Once dried, the alga was kept in the shade. The dried alga was extracted.

### 2.2 Weight - Loss measurement

Measurements of weight changes were performed with rectangular brass specimens. The specimens with same dimensions were immersed in 100 ml of 0.1 N  $\text{H}_3\text{PO}_4$  solutions with and without different concentrations (0.0001 % to 0.0005 %) of PPE and allowed stand for 3 h and 6 h at various temperatures were as follows: 300 K, 318 K, 328 K, and 338 K. At 300 K the specimens were immersed for immersion time of 24, 48, 72, and 96 h. Then, the specimens were rinsed with distilled water and adherent corrosion products for 20 s. then the specimens were rinsed with water, cleaned with acetone and dried. The measurements were conducted for 3 times with different samples. The percentage of inhibition efficiency (IE) over the exposure period was calculated using the following equation (5): [12]

$$\text{IE (\%)} = \frac{W_0 - W_i}{W_0} \times 100 \quad [5]$$

where  $W_0$  and  $W_i$  are the rate of corrosion for brass with and without inhibitor, respectively.

### 2.3 Potentiodynamic Polarization Studies

The potentiodynamic polarization studies were carried out with brass strips having an exposed area of  $1 \text{ cm}^2$ . The cell assembly consisted of brass as working electrode, a platinum foil as counter electrode and a saturated calomel electrode as a reference electrode. Polarization studies were carried out using a potentiostat/galvanostat (Model BAS-100A) at 300 K. The working electrode was immersed in a 0.1 N  $\text{H}_3\text{PO}_4$  and allowed to stabilize for 30 minutes. Each electrode was immersed in a 0.1 N  $\text{H}_3\text{PO}_4$  in the presence and absence of different concentrations of inhibitor to which a current  $1.5 \text{ mA/cm}^2$  was applied for 20 minutes to reduce oxides. The cathodic and anodic polarization curves for brass specimen in the test solution with and without various concentrations of the inhibitor were recorded by scanning the potential range  $\pm 200$  from the corrosion potential at a sweep rate of  $1 \text{ mV/s}$ . The inhibition efficiencies were determined from corrosion currents using the Tafel extrapolation method. The corrosion inhibition efficiency (IE) was calculated from the following equation (6):[12]

$$\text{IE (\%)} = \frac{i_{\text{corr}} - i_{\text{corr(i)}}}{i_{\text{corr}}} \times 100 \quad [6]$$

where  $i_{\text{corr}}$  and  $i_{\text{corr(i)}}$  are the corrosion current density values without and with inhibitor, respectively.

### 2.4 Electrochemical Impedance Spectroscopy

The electrochemical impedance spectroscopy measurements were carried out with well polished brass electrode introduced into 100 ml of test solution using a Solartron electrochemical measurement unit (1280B). After the determination of the steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 mHz and 1 kHz were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potential after 30 minutes of exposure at 300 K. The inhibition efficiencies were determined from charge transfer resistances using the Nyquist representation.

### 2.5 Surface Study

The brass specimen was immersed in 0.1 N  $\text{H}_3\text{PO}_4$  in the presence of 0.0005 % inhibitor for 6 h at 300 K. After 6 h the specimen was taken out and dried. The nature of the film formed on the brass surface was analyzed by FT-IR Perkin Elmer-1600 spectrometer. SEM images were recorded with a Hitachi 3000 H Microscope from the dried film formed on the surface of the brass specimens taken from 0.1 N  $\text{H}_3\text{PO}_4$  in the presence and absence of 0.0005 % inhibitor immersed for 6 h at 300 K.

## 3. RESULTS AND DISCUSSION

### 3.1 Weight-loss method

Table 1 shows the inhibition efficiency (IE) values of brass by weight-loss measurements at different

PPE concentrations in 0.1 N  $\text{H}_3\text{PO}_4$  for different immersion times and temperatures. It has been observed that the inhibition efficiency increases with increase in concentration of SFE and decreases with increase in temperature and immersion time. The maximum IE (84.21 %) of inhibitor was achieved at 0.0005 % of inhibitor at 300 K for 3 h. This result suggests that an increase in extract concentration increases the number of inhibitor molecules absorbed onto the brass surface and reduces the surface area that is available for the direct acid attack on the metal surface [8].

### 3.2 Thermodynamic and Kinetic Analysis

The adsorption of the organic compounds can be described by two main types of interactions: physical adsorption and chemisorptions. They are influenced by the nature of the charge of the metal, the chemical structure of the inhibitor, pH, the type of the electrolyte and temperature [6].

#### 3.2.1 Activation Energy

In order to elucidate the inhibitive properties of the inhibitor and the temperature dependence on the corrosion rates, the energy of activation for the corrosion process in the absence and presence of the inhibitor was evaluated from the following Arrhenius equation (7) and the values obtained are presented in Table 2: [12]

$$\log \frac{p_2}{p_1} = \frac{E_a}{2.303 \times R} \left[ \frac{1}{T_1} - \frac{1}{T_2} \right] \quad [7]$$

where  $p_1$  and  $p_2$  are rate of corrosion at temperatures  $T_1$  and  $T_2$  respectively.

Arrhenius plot for the corrosion rate of brass in the presence PPE for 3 h and 6 h are given in Figure 1: (a)-(b). Straight lines were obtained from the plot of  $\log P$  versus  $1/T$  with slope equal to  $-E_a / 2.303 R$ . Note first that the  $E_a$  values are low, indicating fast corrosion of brass in both the solutions [13]. The estimated values of  $E_a$  for brass corrosion in the presence of PPE are listed in the Table 2. The values of  $E_a > 80 \text{ KJ/mol}$  indicate chemical adsorption where as  $E_a < 80 \text{ KJ/mol}$  infer physical adsorption [14]. The  $E_a$  values indicate that the process is activation controlled. In the present study, the  $E_a$  values support the fact that the inhibitors are physically adsorbed on brass surface. The estimated  $E_a$  in the presence of inhibitor infer that the interaction between the metal surface and the inhibitor was found to be strong enough to reduce corrosion [14]. The  $E_a$  values increase in the presence of PPE is often interpreted as physical adsorption with the formation of an adsorptive film with an electrostatic character [13]. In addition, the  $E_a$  values increases in the same order as the inhibition efficiency. This shows that in the presence of inhibitor the corrosion reaction energy barrier increases in the acid solutions, the corrosion reaction will be further

pushed to surface sites that are characterized by higher values of  $E_a$  indicating that corrosion occurs at the uncovered part of the surface [15].

#### 3.2.2 Free Energy of Adsorption

The free energy of adsorption ( $\Delta G_{\text{ads}}$ ) values were obtained from the following equations and the values are presented in Table 2: [7]

$$\Delta G_{\text{ads}} = -RT \ln (55.5K) \quad [8]$$

where  $K$  is given by

$$K = \frac{\theta}{C(1-\theta)} \quad [9]$$

where  $\theta$  is surface coverage on the metal surface,  $C$  is the concentration of inhibitor in mol/l, and  $K$  is equilibrium constant.

Results obtained indicate that the values of  $\Delta G_{\text{ads}}$  are negative in all cases, indicating that the PPE is strongly adsorbed on the brass surface [15]. The value of  $\Delta G_{\text{ads}}$  indicates that the inhibitor functions by physically adsorbing on the surface of the brass. Generally values of  $\Delta G_{\text{ads}}$  up to the  $-29.53 \text{ KJmol}^{-1}$  are consistent with electrostatic interaction between charged molecules and a charged metal, while those more negative than the  $-40 \text{ KJmol}^{-1}$  involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond [16]. Physical adsorption is a result of electrostatic attraction between charged metal surface and charged species in the bulk of the solution. Adsorption of negatively charged species can also protect the positively charged metal surface acting with a negatively charged intermediate such as acid anions adsorbed on the metal surface [6].

#### 3.2.3 Entropy and Enthalpy

Kinetic parameters such as enthalpy ( $\Delta H$ ) and entropy ( $\Delta S$ ) of activation of corrosion process is calculated from the following thermodynamic basic equations and the values obtained are presented in Table 2: [7]

$$\Delta H = E_a - RT \quad [10]$$

$$\Delta G_{\text{ads}} = \Delta H - T\Delta S \quad [11]$$

Enthalpy of activation of absolute values lower than the  $-24.75 \text{ KJmol}^{-1}$  indicates physical adsorption, and the values approaching  $100 \text{ KJmol}^{-1}$  indicate chemical adsorption [10]. In this study, the values of  $\Delta H$  are lower than the  $-24.75 \text{ KJmol}^{-1}$  confirming physical and spontaneous adsorption on the acid solutions [10]. The negative values of  $\Delta H$  also show that the adsorption of inhibitor is an exothermic process [15].

The  $\Delta S$  values are positive for the acidic baths. This implies that the activation complex is the rate determining step representing association rather than dissociation, indicating that a decrease in disorder takes place on going from reactant to the activated complex [10].

**Table 1. Calculated inhibition efficiency (IE) and surface coverage (SC) values for PPE on brass corrosion in 0.1 N H<sub>3</sub>PO<sub>4</sub> for different immersion temperatures and times**

Conc. of inhibitor (%)	For 3 h		For 6 h		At 300 K	
	SC (θ)	IE (%)	SC (θ)	IE (%)	SC (θ)	IE (%)
300 K					24 Hours	
0.0000	0	0	0	0	0	0
0.0001	0.4736	47.36	0.3077	30.77	0.3247	32.47
0.0002	0.5263	52.63	0.3846	38.46	0.3507	35.07
0.0003	0.5790	57.90	0.4231	42.31	0.3896	38.96
0.0004	0.7368	73.68	0.5385	53.85	0.4416	44.16
0.0005	0.8421	84.21	0.6923	69.23	0.5065	50.65
318 K					48 Hours	
Blank	0	0	0	0	0	0
0.0001	0.4286	42.86	0.2424	24.24	0.2360	23.60
0.0002	0.4762	47.62	0.3333	33.33	0.2528	25.28
0.0003	0.5238	52.38	0.3939	39.39	0.2697	26.97
0.0004	0.6666	66.66	0.4849	48.49	0.3202	32.02
0.0005	0.7143	71.43	0.5758	57.58	0.3989	39.89
328 K					72 Hours	
Blank	0	0	0	0	0	0
0.0001	0.3750	37.50	0.1964	19.64	0.1983	19.83
0.0002	0.4167	41.67	0.2500	25.00	0.2236	22.36
0.0003	0.5000	50.00	0.2857	28.57	0.2363	23.63
0.0004	0.6250	62.50	0.3214	32.14	0.2827	28.27
0.0005	0.6666	66.66	0.4286	42.86	0.3418	34.18
338 K					96 Hours	
Blank	0	0	0	0	0	0
0.0001	0.2353	23.53	0.1940	19.40	0.1489	14.89
0.0002	0.2647	26.47	0.2239	22.39	0.1641	16.41
0.0003	0.4118	41.18	0.2537	25.37	0.1763	17.63
0.0004	0.5000	50.00	0.2985	29.85	0.2097	20.97
0.0005	0.6177	61.77	0.4030	40.30	0.2675	26.75

**Table 2. Calculated activation energy (E<sub>a</sub>), free energy of adsorption (ΔG<sub>ads</sub>), enthalpy change (ΔH), entropy change (ΔS) values for PPE on brass corrosion in 0.1 N H<sub>3</sub>PO<sub>4</sub> at 300 K**

Conc. of inhibitor (%)	E <sub>a</sub> from Eq. (1) (kJ/mol)	E <sub>a</sub> from Arrhenius Plot (kJ/mol)	ΔG <sub>ads</sub> (kJ/mol)	ΔH (kJ/mol)	ΔS (mol/kJ)
For 3 Hours					
Blank	12.91	12.98	0	0	0
0.0001	21.20	19.15	-29.53	-24.75	0.0159
0.0002	22.67	23.94	-27.80	-24.70	0.0103
0.0003	20.33	29.46	-26.73	-24.64	0.0070
0.0004	27.15	31.92	-25.44	-24.62	0.0027
0.0005	32.54	35.90	-23.94	-24.58	0.0013
For 6 Hours					
Blank	21.00	16.76	0	0	0
0.0001	24.38	22.53	-29.13	-24.71	0.0147
0.0002	26.15	25.34	-27.67	-24.68	0.0100
0.0003	26.72	26.60	-26.73	-24.67	0.0069
0.0004	30.30	27.93	-26.06	-24.66	0.0047
0.0005	35.71	34.82	-25.12	-24.59	0.0018

**Table 3. Calculated rate constant and half-life period values for PPE on brass corrosion in 0.1 N H<sub>3</sub>PO<sub>4</sub> at 300 K**

Conc. of inhibitor (%)	Rate constant (sec <sup>-1</sup> )	Half-life Period (sec)
0.0001	0.5654	1.2257
0.0002	0.5758	1.2037
0.0003	0.5758	1.2037
0.0004	0.6142	1.1283
0.0005	0.6142	1.1283

**Table 4. Electrochemical parameters and inhibition efficiency (IE) for corrosion of brass in 0.1 N H<sub>3</sub>PO<sub>4</sub> containing different concentrations of PPE**

Conc. of inhibitor (%)	OCP (mV) vs. SCE	E <sub>corr</sub> (mV) vs. SCE	Tafel constants		i <sub>corr</sub> (μA/cm <sup>2</sup> )	IE (%)
			b <sub>a</sub> (mV/dec)	b <sub>c</sub> (mV/dec)		
Blank	-193	-190	300	100	310	0
0.0001	-216	-220	260	115	220	29.32
0.0002	-232	-230	160	120	200	35.48
0.0003	-242	-240	140	130	150	51.61
0.0004	-250	-252	130	138	130	58.07
0.0005	-260	-260	85	150	63	82.74

**Table 5. AC Impedance parameters for corrosion of brass in 0.1 N H<sub>3</sub>PO<sub>4</sub> containing different concentrations of PPE at 300 K**

Conc. of inhibitor (%)	R <sub>t</sub> (ohmcm <sup>2</sup> )	C <sub>dl</sub> (μF/cm <sup>2</sup> )	IE (%)
Blank	150.60	5.74	00.00
0.0001	320.61	3.22	53.03
0.0002	424.95	2.61	64.56
0.0003	502.46	2.31	70.02
0.0004	629.75	1.99	76.09
0.0005	1400.11	1.18	84.24

### 3.2.4 Rate Constant and Half Life

Figure 2 show the plots of log W<sub>f</sub> (final weight loss) obtained in weight-loss studies vs. time in days for the brass dissolution. From the plots, the values of rate constant and half-life were evaluated using the following equations and the values obtained are presented in Table 3: [11, 17]

$$\text{Rate constant (k)} = 2.303 \times \text{slope (sec}^{-1}) \quad [12]$$

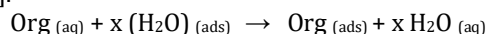
$$\text{Half - life period } t_{1/2} = \frac{0.693}{k} (\text{sec}) \quad [13]$$

In this study, linear plots were obtained, which indicates first order kinetics [9]. In this study the rate constant values were decreased where as the half-life values were increased with increasing concentration of PPE.

### 3.2.5 Adsorption Isotherms

The values of surface coverage  $\theta$  for different

concentrations of the PPE at 300 K have been used to identify the best isotherm to determine the adsorption process. The adsorption of organic adsorbate on the surface of copper is regarded as substitutional process between the organic compound in the aqueous phase org<sub>aq</sub> and the water molecules adsorbed on the copper surface (H<sub>2</sub>O)<sub>ads</sub> [18].



where x is the size ratio, that is the number of water molecules displaced by one molecule of organic inhibitor. Attempts were made to fit  $\theta$  values of various isotherms, including Langmuir, Freundlich, Temkin and Frumkin isotherms. By far the results were best fitted by Temkin adsorption isotherm. The Temkin adsorption isotherm is given by the following equation.

$$\ln kC = a\theta \quad [14]$$

Selva Kumar et al.,



where  $k$  is the equilibrium constant of the adsorption reaction,  $C$  is the inhibitor concentration in the bulk of the solution and  $a$  is the molecule interaction parameters depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the metal surface. The plot of  $\theta$  against  $\log C$  for all additives gives straight lines, as shown in Figure: 3 (a)-(b). This indicates that these compounds are adsorbed on the surface of brass according to Temkin adsorption isotherm [19,20].

### 3.3 Potentiostatic Polarization Studies

Polarization measurement is an important research tool in the investigation of a variety of electrochemical phenomena. Such measurements permit studies of the reaction mechanism and the kinetics of corrosion phenomena on the metal deposition. Figure 4 shows the cathodic and anodic polarization curves of brass in 0.1 N  $H_3PO_4$  with and without addition different concentrations of PPE. Table 4 gives the values of associated electrochemical parameters. The  $i_{corr}$  values decreased with increasing concentration of inhibitor. The values of anodic Tafel slope ( $b_a$ ) and cathodic Tafel slope ( $b_c$ ) of PPE added solutions are found to change with inhibitor concentration, which clearly indicates that the inhibitors controlled both the anodic and cathodic reactions. Thus this inhibitor acted as a mixed type inhibitor [8]. The IE of PPE attained a maximum value at 0.0005 % concentration of inhibitor. The values of IE increased with increasing concentration of inhibitor, indicating that a higher surface coverage was obtained in solution with high concentration of inhibitor. The effect of the anodic polarization behavior of brass (Figure 4) suggests that protective films formed on the metal surface can alter anodic dissolution in solution shows that PPE formed a film that acted as a barrier to protect the metal surface [19-21].

### 3.4 AC Impedance Measurements

AC impedance spectroscopy has been shown to be a powerful tool to study the corrosion process of metals in different environments and to characterize the inhibition ability of a corrosion inhibitor, which is related to the charge transfer resistance ( $R_{ct}$ ). The double layer capacitance ( $C_{dl}$ ) can also be used to determine the inhibition ability. The corrosion behavior of brass, in acidic solution with and without PPE, is also investigated by AC impedance measurements at 300 K. The impedance diagrams were given in the Nyquist representation (Figure 5) which can be modeled as an electric equivalent circuit (Figure 6). From the Nyquist plot, the charge transfer resistance ( $R_{ct}$ ) and double layer capacitance ( $C_{dl}$ ) values were calculated. The inhibition efficiency (IE %) from the electrochemical impedance measurement was calculated using the following equation (15): [5]

$$IE(\%) = \frac{R_{ct(i)} - R_{ct}}{R_{ct(i)}} \times 100 \quad [15]$$

where  $R_{ct}$  and  $R_{ct(i)}$  are the charge transfer resistance in the absence and presence of inhibitor respectively.

The impedance parameters and the IE % derived from the investigation are mentioned given in Table 5. As it can be seen from impedance diagrams (Figure 5) show a semi-circular appearance, indicating that a charge transfer process mainly controls the corrosion of brass. From the impedance data, we notice an increase in the charge transfer resistance and decrease of the double layer capacitance with increasing the inhibitor concentration, indicating that PPE inhibits the corrosion rate of brass by an adsorption mechanism. Therefore, the decrease in the  $C_{dl}$  value can be attributed to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggesting that the inhibitor molecules act by adsorption at the metal/solution interface as a consequence of the replacement of water molecules by the inhibitor molecules [8].

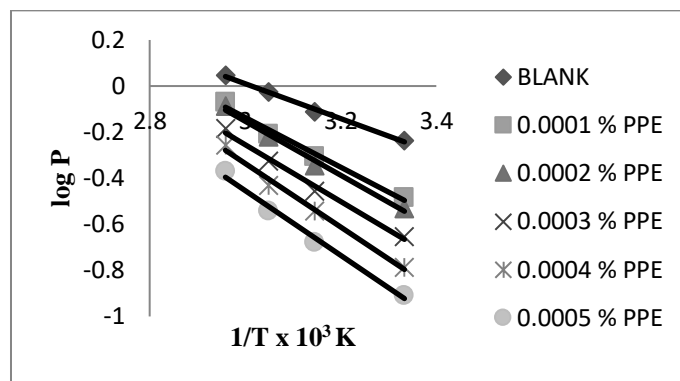
A comparison may be made between the inhibition efficiency values obtained by different methods (weight loss, potentiostatic polarization and AC impedance methods). We can see that whatever the method used, no significant changes are observed in IE % values. We can then conclude that there is a same trend follows with the three methods used in this study at all tested concentrations and that the acid extract of *Padina pavonica* acts as inhibitor for acid corrosion of brass.

### 3.5 Characterization of *Padina pavonica* Extract and Surface Analysis

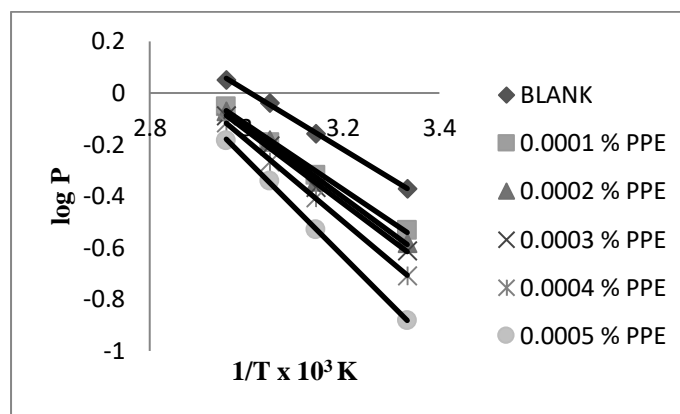
#### 3.5.1 FT-IR spectroscopy

Figure 7 shows the FT-IR spectra recorded in the range 400-4000  $cm^{-1}$  to identify the functional groups present in PPE. From FT-IR, It was observed that aromatic molecules with following functional groups, Intermolecular hydrogen bonding and O-H stretching (3388.93  $cm^{-1}$ ), -C-C stretching in ring aromatics (1417.68  $cm^{-1}$ ), -C-N stretching in aliphatic amines (1022.27  $cm^{-1}$ ), -C-H bending in alkenes (875.68  $cm^{-1}$ ), -C-H rocking in alkanes (721.38  $cm^{-1}$ ) and -S=S stretching in aryl disulfides (447.49  $cm^{-1}$ ) are present in PPE.

The chemical analysis of PPE found that organic aromatic molecules, aromatic esters, amines, alkaloids, flavonoids, terpenoids, phenols and sulfur containing compounds are present in it. Further found that PPE inhibits the corrosion of brass specimen with high efficiency due to the presence of N, S and O in the organic molecules of PPE [22,23].



(a)



(b)

Figure 1: Arrhenius plot for 0.1 N H<sub>3</sub>PO<sub>4</sub> with different concentrations of PPE for different times

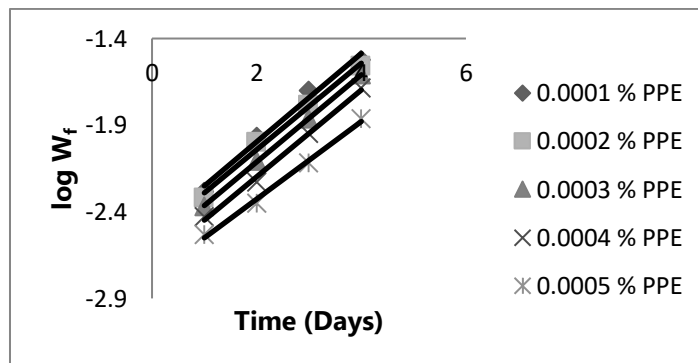
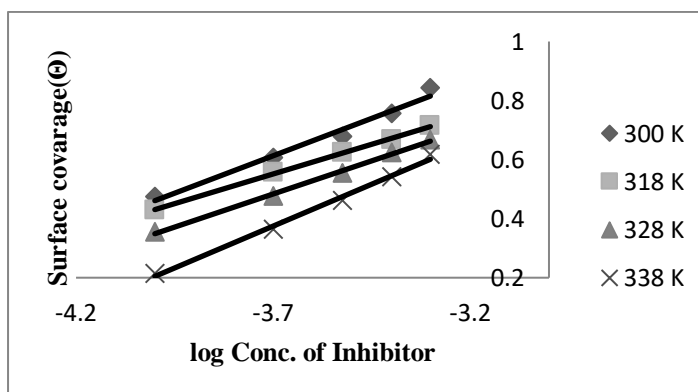


Figure 2: Plot of log  $W_f$  vs. time (days) for 0.1 N H<sub>3</sub>PO<sub>4</sub> with different concentrations of PPE



(a)

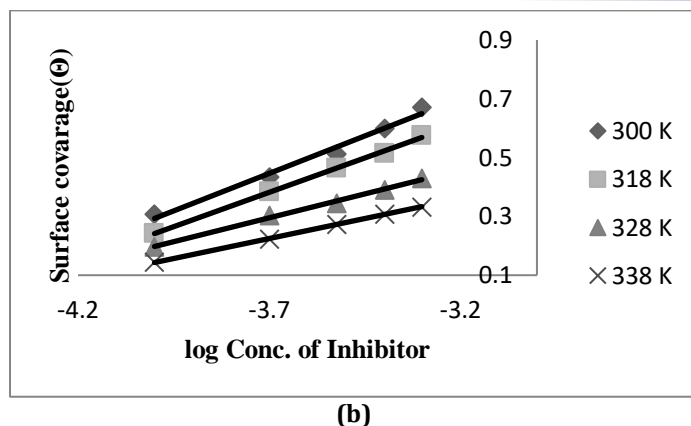


Figure 3: Temkin's adsorption isotherm plot for 0.1 N  $\text{H}_3\text{PO}_4$  with different concentrations of PPE for different times

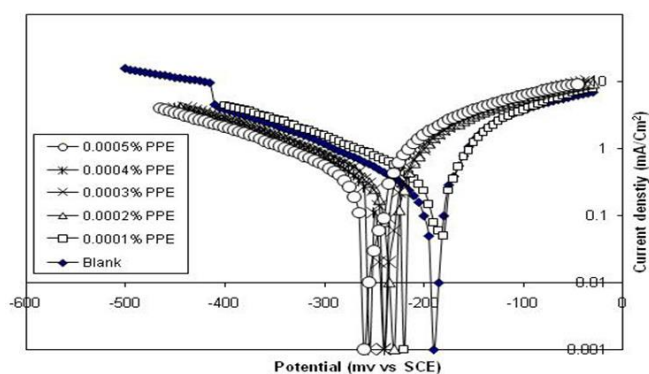


Figure 4: Polarization curves for brass in 0.1 N  $\text{H}_3\text{PO}_4$  with different concentrations of PPE

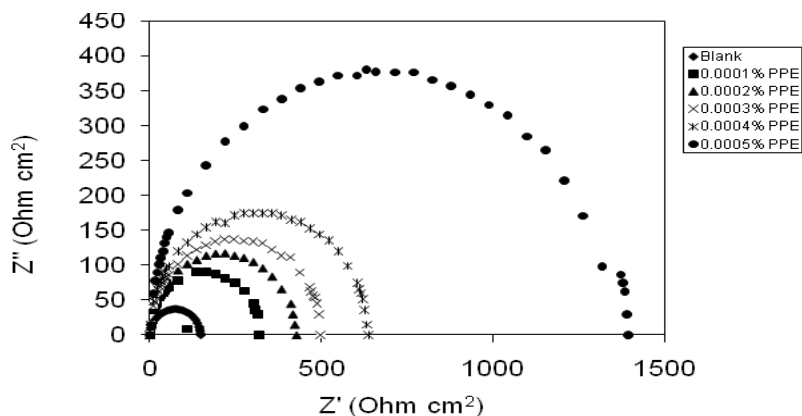


Figure 5: Nyquist plots of brass in 0.1N  $\text{H}_3\text{PO}_4$  with different concentrations of PPE

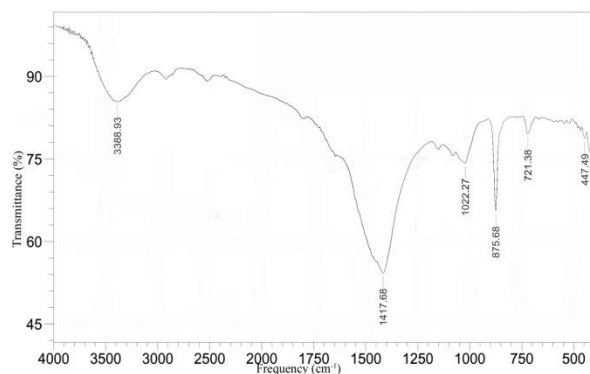


Figure 6: FT-IR spectra of the surface of brass formed by immersing sample in 0.1 N  $\text{H}_3\text{PO}_4$  with PPE for 6 h



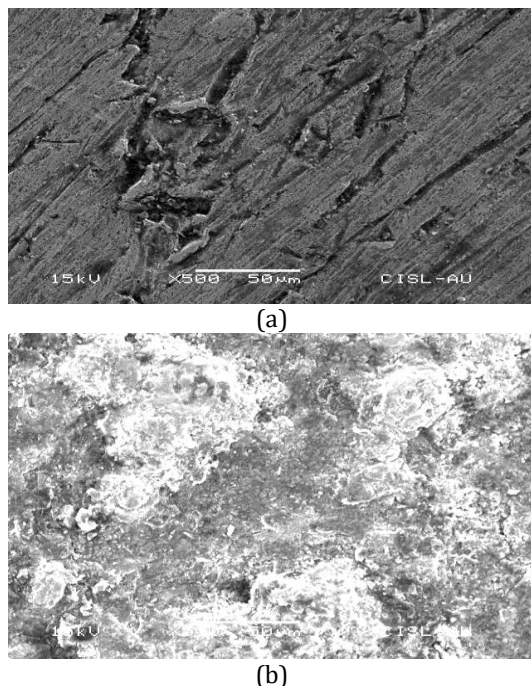


Figure 7: SEM images of brass surface after 6 h immersion in 0.1N H<sub>3</sub>PO<sub>4</sub> in the absence (a) and presence (b) of PPE.

### 3.5.2 Scanning Electron Microscopy

SEM micrograms of the polished surface of brass exposed for 6 h in 0.1 N H<sub>3</sub>PO<sub>4</sub> in absence and presence of 0.0005 % PPE are shown in Figure: 8 (a)-(b) shows the surface morphology of brass formed in 0.1 N H<sub>3</sub>PO<sub>4</sub> without and with PPE. In the comparison of the SEM micrograms, there were a smooth surface on brass in absence of extract and a rough surface with deposited extract in presence of the PPE. This confirms that the extract inhibited corrosion of brass through adsorption of the inhibitor molecules on metal surface. After immersing in the inhibitor containing solution, the entire metal surface was covered with a layer formed with inhibitor as a barrier to corrosion, as denoted by rougher over abrasions [7]. The inhibiting layer was possibly consisting of Cu<sup>2+</sup> and Zn<sup>2+</sup> complexes formed with the PPE derivatives are mentioned in FT-IR [24].

### 4. CONCLUSION

The inhibition efficiency of PPE on corrosion of brass in 0.1 N H<sub>3</sub>PO<sub>4</sub> increases on increasing of concentration of the extract and decreases with rise in temperature. Adsorption of inhibitor molecules of the extract on brass surface is found to obey Temkin adsorption isotherm. The increase in the values of activation energies of the corrosion process in the presence of extract indicates that PPE creates a physical barrier to charge and mass transfer, leading to reduction in corrosion rate of brass in 0.1 N H<sub>3</sub>PO<sub>4</sub>. The negative values of  $\Delta G_{ads}$  and  $\Delta H$  highlight that the inhibition of corrosion of brass through adsorption is spontaneous and exothermic. Their values also reveal that physical adsorption is involved in the adsorption process. Potentiodynamic polarization

measurements show that PPE acts as a mixed type inhibitor. Inhibition efficiency values were show a same trend follows with weight-loss, potentiodynamic polarization and electrochemical impedance spectroscopy studies. The inhibitive effect could be attributed to the phytochemical constituents present in the inhibitor containing N, S, O atoms. SEM and FT-IR studies confirm that corrosion inhibition of brass in 0.1 N H<sub>3</sub>PO<sub>4</sub> is due to adsorption of the PPE on brass surface.

### REFERENCES

- [1]. Chandrasekaran, V., Kannan, K., Natesan, M., 2005. Inhibiting properties of some amines on corrosion behaviour of mild steel in phosphoric acid solution at various temperatures, Asian Journal of Chemistry. 17 (3), 1921-1934.
- [2]. Chandrasekaran, V., Kannan, K., Natesan M., 2005. Electrochemical behaviour and inhibiting properties of isopropyl amine on mild steel corrosion in phosphoric acid solution, Oriental Journal of Chemistry. 21 (1), 81-88.
- [3]. Ranjana, Nandi M. M., 2011. Evaluating two new sulphonamidoimidazolines on the corrosion of brass in 0.6 N aqueous sodium chloride solution, Indian Journal of Chemical Technology. 18, 29-36.
- [4]. Ranjana, Ranu Banerjee, Nandi, M. M., 2012. Corrosion inhibition of brass in presence of 1,4,5,6- tetrahydropyrimidine derivatives in chloride solution, Indian Journal of Chemical Technology. 20, 237- 244.

- [5]. Ravichandran, R., Rajendran, N., 2005. Electrochemical behavior of brass in artificial seawater: effect of organic inhibitors, *Applied Surface Science*, 241, 449-458.
- [6]. Vijayalakshmi, P. R., Rajalakshmi, R., Subhashini S., 2011. Corrosion inhibition of aqueous extract of *Cocos nucifera*- coconut palm-petiole extract from destructive distillation for the corrosion of mild steel in acidic medium, *Portugaliae Electrochimica Acta*, 29 (1), 9- 21.
- [7]. Ramananda, Mayanglambam, S., Vivek Sharma, Gurmeet Singh, 2012. *Musa Paradisiaca* Extract as a green inhibitor for corrosion of mild steel in 0.5 M sulphuric acid solution, *Portugaliae Electrochimica Acta*. 29 (6), 405-417.
- [8]. Khadraoui, A., Khelifa, A., Boutoumi, H., Mettai, B., Karzazi, Y., Hammouti, B., 2014. Corrosion inhibition of carbon steel in hydrochloric acid solution by *Mentha Pulegium* Extract, *Portugaliae Electrochimica Acta*. 32 (4), 271-280.
- [9]. Ejikeme, P. M., Umana, S. G., Onukwuli, O. D., 2012. Corrosion inhibition of aluminium by *Treculia Africana* leaves extract in acid medium, *Portugaliae Electrochimica Acta*. 30 (5), 317-328.
- [10]. Muna K. Irshadat, Eyad M. Nawafleh, Tareq T. Bataineh, Riyadh Muhaidat, Mahmoud A. Al-Qudah, Ahmed A. Alomary, 2011. Investigation of the inhibition of aluminium corrosion in 1 M NaOH solution by *Lupinus varius* l. extract, *Portugaliae Electrochimica Acta*. 31 (1), 1-10.
- [11]. Ravichandran, R., Rajendran, N., 2014. Electrochemical behavior of brass in artificial seawater: effect of organic inhibitors, *Applied Surface Science*. 241, 449-458.
- [12]. Chandrasekaran, V., Selva Kumar, R., 2015. *Sargassum wightii* Extract as a Green Inhibitor for Corrosion of Brass in 0.1 N Phosphoric Acid Solution, *Oriental Journal of Chemistry*. 31 (2), 939-949.
- [13]. Chandrasekaran, V., Saravanan, J., 2006. Effect of S-AITA on mild steel Corrosion in Acidic Medium, *Corrosion Science and Technology*. 5(5), 160.
- [14]. Mahmoud, S. S, 2006. Corrosion inhibition of Muntz (63% Cu, 37% Zn) alloy in HCl solution by some naturally occurring extracts, *Portugaliae Electrochimica Acta*. 24, 441-445.
- [15]. Elmsellem, H., Basbas, N., Chetouani, A., Aouniti, A., Radi, S., Messali, M., Hammouti, B., 2014. Quantum chemical studies and corrosion inhibitive properties of mild steel by some pyridine derivatives in 1 N HCl solution, *Portugaliae Electrochimica Acta*. 32 (2), 77-108.
- [16]. Tadeja Kosec, Ingrid Milosev, Boris Pihlar, 2014. Benzotriazole as an inhibitor of brass corrosion in chloride solution, *Applied Surface Science*. 253, 8863-8873.
- [17]. Chandrasekaran, V., Kannan, K., Natesan, M., 2005. The Effect of Imidazole and 2-Methyl Imidazole on the Corrosion of Mild Steel in Phosphoric acid solution, *Corrosion Science Technology*. 4 (5), 191-200.
- [18]. Megahed, H. E., 2011. Ethoxylated fatty esters as corrosion inhibitors for copper in nitric acid solutions, *Portugaliae Electrochimica Acta*. 29(4), 287-294.
- [19]. Chandrasekaran, V., Gokulalakshmi, K., 2006. Corrosion studies on brass in H<sub>3</sub>PO<sub>4</sub> with Benzamide, *Bulletin of Electrochemistry*. 22, 379-384.
- [20]. Chandrasekaran, V., Selva Kumar, R., 2016. *Valoniopsis pachynema* Extract as a Green Inhibitor for Corrosion of Brass in 0.1 N Phosphoric Acid Solution, *Metallurgical and Materials Transactions B*. 47(2), 891-898.
- [21]. Gaikwad, A. B., Patil, P.P., Sudeshna Chaudhari, 2012. Poly (o-anisidine) coatings on brass: Synthesis, characterization and corrosion protection, *Current Applied Physics*. 9(1), 206-218.
- [22]. Ravichandran, R., Nanjudan, S., Rajendran, N., 2004. Influence of benzotriazole derivatives on the dezincification of 65-35 brass in sodium chloride solution, *Applied surface Science*. 236, 241-250.
- [23]. Du, X.S., Su, Y.J., Li, J.X., Qiao, L.J., Chu, W.Y., 2012. Inhibitive effects and mechanism of phosphates on the stress corrosion cracking of brass in ammonia solutions, *Corrosion Science*. 60, 69-75.
- [24]. Khadraoui, A., Khelifa, A., Boutoumi, H., Mettai, B., Karzazi, Y., Hammouti, B., 2014. Corrosion Inhibition of Carbon Steel in Hydrochloric Acid Solution by *Mentha Pulegium* Extract, *Portugaliae Electrochimica Acta*. 32(4), 271-280.